MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

AD-A152 233

Luminescence Probe Studies of Ionomers. II. Steady-State Measurements from Sulfonated Polyethylene and Teflon Membranes.

by

Marilyn N. Szentirmay, Nelson E. Prieto and Charles R. Martin

Prepared for Publication

in

Talanta
(Honorary Issue for Henry Freiser)

Department of Chemistry
Texas A&M University
College Station, Texas

February 3, 1985

DTIC
SELECT
APR 1 0 1985
S
A

85 03 22 012

DTIC FILE COPY

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report #9	2. GOVT ACCESSION NO. AD-A152 233	3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) Luminescence Probe Studies of Ionomers. II. Steady-State Measurements from Sulfonated Polyethylene and Teflon Membranes.	5. TYPE OF REPORT & PERIOD COVERED Technical Report
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) Marilyn N. Szentirmay, Nelson E. Prieto, Charles R. Martin	8. CONTRACT OR GRANT NUMBER(s) N00014-82K-0612

9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Texas A&M University College Station, Tx. 77843	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 627-838

11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	12. REPORT DATE February 3, 1985
	13. NUMBER OF PAGES 7

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ion Exchange Membranes, Luminescence Probe Studies, RAI Membranes.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Luminescence probe studies of sulfonated Teflon and sulfonated polyethylene ionomer membranes are described. These membranes were obtained from RAI Research Corporation of Hauppauge, N.Y. and were prepared via radiation grafting sidechains onto preformed Teflon and polyethylene sheets. The intent of these investigations was to determine how the membrane water content and the nature of the counterion affect the chemical characteristics of the ionic cluster phases in these ionomers. Three luminescent molecules, pyrene, $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine), and a quaternary ammonium-containing

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-LF-014-6601

20. ABSTRACT (continued)

dansyl derivative were used to probe the cluster microenvironment. We have found that the cluster micropolarity is quite dynamic, being close to aqueous-like when the membrane water content is high and extremely nonpolar when the water content is low. These studies also suggest that mainchain material intrudes into the ionic cluster.

Accession For

NTIS GRA&I

DTIC TAB

Unannounced

Justification

By

Distribution/

Availability Codes

Avail and/or

Dist   Special

Luminescence Probe Studies of Ionomers. II. Steady-State Measurements
from Sulfonated Polyethylene and Teflon Membranes

Marily N. Szentirmay, Nelson E. Prieto and Charles R. Martin*

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Summary

Luminescence probe studies of sulfonated Teflon and sulfonated polyethylene ionomer membranes are described. These studies have shown that the micropolarities of the ionic clusters within these ionomers are quite dynamic, varying with the nature of the chain material and the membrane water content. These studies also suggest that polymer chain material intrudes into the ionic cluster phase.

Introduction

Ion-containing polymers, or ionomers (1,2), are used in a variety of chemical and electrochemical processes and devices including fuel cells (3), solar energy conversion systems (4), batteries (5), chemically modified electrodes (6) and industrial electrolytic processes (7). Because of their technological importance, a broad arsenal of chemical methodologies is currently being used to study the chemical and morphological properties of these polymers (8-12). This research effort has shown that the charged groups in ionomers can aggregate to form micelle-like domains called ionic clusters. The structural and chemical details of these microdomains have not yet been elucidated.

Because luminescence probe methods have proven useful in studies of micelles (13) and other chemical microdomains, we and others have been using luminescence methods to study ionomers (14-16). We have recently examined the micropolarity of the ionic clusters in Nafion, a perfluorosulfonate ionomer, by following changes in the luminescence properties of incorporated probes (16). The micropolarity varied significantly depending on the water content and the counterion type (16). These results are valuable in that the polarity of Nafion, as reported by the luminescent probe, can be used to predict the chemical properties of the microenvironment around other molecules or ions (e.g., electroactive species, catalysts, diffusants) incorporated into the membrane. These data can in turn aid in the prediction or interpretation of the rates and courses of chemical and electrochemical processes occurring within the membrane (16). For example, by using the results of luminescence probe experiments, we have recently succeeded in changing the redox potential of ferrocene in a Nafion film at an electrode surface by adjusting the film

polarity through incorporation of a hydrophobic counterion (16).

Ionomers prepared by grafting styrenesulfonate sidechains onto sheets of hydrocarbon or fluorocarbon polymers are proving to be important membrane materials (17). For this reason, we have used luminescence probe experiments to study the chemical and morphological properties of styrenesulfonate-grafted Teflon and polyethylene membranes. The results of these studies are reported here.

Experimental Section

Materials. Sulfonated polyethylene (PE-SS, 700 g per mole -SO_3H) and sulfonated polytetrafluoroethylene (PFE-SS 850 g per mole -SO_3H) were donated by RAI Research Corporation (Hauppage, NY). These polymers are prepared by radiation grafting styrene sidechains onto preformed Teflon or polyethylene sheets; the sidechains are then sulfonated using H_2SO_4 (17). 5-Dimethylaminonaphthalene-1-sulfonamidoethyl-trimethylammonium perchlorate ($DAClO_4$) was obtained from Sigma. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (bpy = 2,2'-bipyridine) was obtained from G. F. Smith. Pyrene (Py) (99+%) and CsOH were obtained from Aldrich. All other chemicals were of reagent grade. Water was either triply distilled or circulated through a Milli-Q water purification system (Millipore Corp.).

Procedures. PFE-SS was cleaned ultrasonically in ethanol for 4 h. PE-SS was cleaned ultrasonically in 50:50 ethanol-water for 1 h. After cleaning, all membranes were boiled in water for 4 h. Membranes in various counter-ionic forms were prepared by soaking the H^+-form membranes in concentrated solutions of the appropriate metal hydroxide. Excess base was then removed by stirring the membranes in several portions of pure water. The luminescent probes (Py, DA^+, $Ru(bpy)_3^{2+}$) were incorporated (loaded) by stirring the membranes in aqueous solutions of the probes. The quantity

of probe incorporated was determined spectrophotometrically (16); loading levels were kept low (DA^+ and $Ru(bpy)_3^{2+}$ less than 3 probes ions per 100 $-SO_3^-$ sites, Py ca. 0.3 probe molecules per 100 $-SO_3^-$ sites) so as to minimize the effect of the probe on the membrane microenvironment.

The effects of membrane water content on the emission characteristics of the probes were investigated by gradually drying the membranes, first by exposure to air, then in a desiccator, and finally in a vacuum oven (temperature $<70°C$). The water content of each membrane was determined from the average of weights recorded immediately before and after each spectrum was acquired. Water content is reported as percent by weight (100 x wt. H_2O/wt. dry polymer) and as the number of water molecules per $-SO_3^-$ site. Membranes dried in a vacuum oven at 100°C for 1 to 3 days served as "zero" water content references (16).

Spectroscopy. Emission spectra were obtained with a Spex Fluorolog 2 spectrofluorometer. The Spex solid sample holder with front surface viewing geometry was used. Excitation wavelengths for Py, $Ru(bpy)_3^{2+}$ and DA^+ were 310 nm, 445 nm, and 340 nm unless otherwise noted. Emission slit widths of 0.8 nm (Py spectra) and 4.1 nm ($Ru(bpy)_3^{2+}$ and DA^+ spectra) were used. Absorption spectra were recorded on a Beckman Model 26 spectrophotometer. PFE-SS does not absorb light of wavelengths greater than 350 nm and no PFE-SS emission was detected from the excitation wavelengths used here. In contrast, PE-SS absorbs light of wavelengths less than 400 nm and shows an absorbance maximum at 374 nm. PE-SS also emits weakly when excited at any of the wavelengths used in these studies.

The spectroscopic characteristics of PE-SS are both enigmatic and undesirable. A polyethylene film containing styrenesulfonate groups would not be expected to absorb light at wavelengths above ca. 300 nm suggesting

the presence of some impurity. This impurity cannot, however, be cleaned from the membrane using conventional membrane pretreatment procedures (14,16,18). This suggests that the impurities might be covalently attached and that they might result from damage incurred during the grafting or sulfonation steps. The spurious absorbance/emission of PE-SS is undesirable because it represents an interference in the analysis of the probe's luminescence data. This interference precluded the use of Py as a probe in PE-SS and makes the interpretation of the effect of drying on DA^+ emission in PE-SS difficult.

Results and Discussion

Luminescent Probes. Three luminescent molecules, Py, DA^+ and $Ru(bpy)_3^{2+}$, were chosen as probes of the microenvironments within the radiation grafted membranes. As discussed in detail in our previous paper (16), these probes were chosen because the effects of environment polarity on their emission characteristics have been extensively studied. Briefly, emission spectra of pyrene contain partly resolved vibronic bands whose relative intensities vary with solvent polarity (19). In general, an increase in solvent polarity results in a decrease of the ratio of the third to the first vibronic band intensities (I_3/I_1) (19). Derivatives of dimethylaminonaphthalenesulfonate (DNS) such as DA^+ have been used as polarity probes for a number of chemical systems (20). The wavelengths of maximum emission intensity (λ_{Max}) for 1,5-DNS derivatives are sensitive to solvent polarity, blueshifting with decreasing polarity (20). The fluorescence quantum yields for 1,5-DNS derivatives are also solvent sensitive, with water producing one of the lowest quantum yields (20).

The emission characteristics of $Ru(bpy)_3^{2+*}$ have been studied extensively (21). $Ru(bpy)_3^{2+*}$ emission energies do not correlate well

with solvent polarity (16). However, our luminescence probe studies of aqueous solutions of Nafion polyelectrolytes have shown that increasing emission energies and quantum yields result when $Ru(bpy)_3^{2+}$ is taken from a purely aqueous environment to an environment where interaction with fluorocarbon chain material is possible (15). A similar effect is observed when $Ru(bpy)_3^{2+}$ is placed in fluorocarbon micelles (22) or in Nafion membranes (14,16). In contrast, the emission energies of $Ru(bpy)_3^{2+*}$ in long-chain alcohols or hydrocarbon micelles are less than that for $Ru(bpy)_3^{2+*}$ in water. These results suggest that $Ru(bpy)_3^{2+}$ is sensitive to the nature of its chemical environment and, of particular interest to this study, can discriminate between hydrocarbon and fluorocarbon-containing environments. The effects of various solvents on the emission characteristics of the probes used here are shown in Table I.

Emission from Fully Hydrated Membranes. Luminescence probe studies of Nafion membranes have shown that the polarity of the microenvironment around a probe molecule or ion is an average of contributions from the components which constitute the microenvironment (14,16). Hence, if the environment around a probe is essentially aqueous, the probe should report back a λ_{Max} or I_3/I_1 equivalent to that for the probe in water. Conversely, if the immediate environment contains both water and chain material, an environment polarity significantly lower than that of a bulk aqueous phase will be experienced and reported by the probe. This was the case when the probes used here were incorporated into Nafion (16).

Table II shows that the water contents of the fully hydrated (boiled 4 h.) PE-SS membranes are extremely high, much higher than both Nafion (40% H_2O (16)) and PFE-SS. In spite of these very high water contents, λ_{Max} for DA^+ in PE-SS is blushifted relative to its λ_{Max} in water; however,

the extent of the blueshift is much less than that observed in Nafion, PFE-SS or a relatively nonpolar hydrocarbon solvent (see Table I). These data suggest that, as was the case with Nafion, DA^+ is experiencing an effective microenvironment polarity which is made up of contributions from water and chain material, and because of the relatively high water contents, the polarity is much higher than that for DA^+ in either Nafion or PFE-SS.

The PFE-SS studied here contains significantly more $-SO_3H$ sites per gram than Nafion. It is, therefore, somewhat surprising that PFE-SS contains much less water than Nafion. These lower water contents may result from the higher crystallinity of the Teflon-based PFE-SS membrane (23). In perfect agreement with the arguments presented above, both DA^+ and Py report back microenvironment polarities which are much lower than those for these probes in either PE-SS or Nafion (16). In the case of Py, this agreement may be fortuitous because drying experiments have shown that Py's microenvironment in PFE-SS is insensitive to changes in water content (vide infra).

As noted above, $Ru(bpy)_3^{2+}$ can apparently differentiate between a hydrocarbon and a fluorocarbon environment. This is evident in the data shown in Table II in that $Ru(bpy)_3^{2+}$'s emission is redshifted (relative to water) in PE-SS and blueshifted in PFE-SS. These data, again, indicate that the probe has access to the chain material. More importantly, the PFE-SS data indicate that $Ru(bpy)_3^{2+}$ interacts with the fluorocarbon main chain more extensively than with the aromatic hydrocarbon sidechain.

Experimental evidence suggests that, in analogy to Nafion and other ionomers (24), the $-SO_3^-$ sites, their counterions and the water of

hydration for each are aggregated into ionic clusters in PFE-SS (25,26). Most recent models of ionomer clustering predict clusters which are devoid of chain material and which are lined with the ionic sites (27,28). The hydrocarbon sidechains in PFE-SS, which contain the $-SO_3^-$ groups, are of sufficient length (3 to 10 repeat units (29)) that a cluster having a structure of this type would have hydrocarbon walls. This would preclude or at least greatly hinder $Ru(bpy)_3^{2+}$-fluorocarbon interactions. The $Ru(bpy)_3^{2+}$ emission data from PFE-SS strongly suggests, then, that chain material intrudes into the ionic cluster. It is of interest to note that Eisenberg has proposed a model which allows for main chain penetration into the cluster (30) and that both infra red (12) and transport (6) studies of Nafion provide evidence which supports this model.

Effect of Water Content on Microenvironment-Polarity. If the properties of a probe's microenvironment are determined by the relative concentrations of water and chain material, then the polarity of this environment should decrease as water is removed from the membrane. All of the probes used here reported back decreasing microenvironment polarities when water was removed from Nafion membrane (16). In contrast, the polarity changes observed on removal of water from PFE-SS and PE-SS depended on the probe used. DA^+ in PFE-SS and $Ru(bpy)_3^{2+}$ in both PFE-SS and PE-SS behaved in the expected manner. As water was removed from PFE-SS, DA^+'s and $Ru(bpy)_3^{2+}$'s λ_{Max} values blueshifted (Figures 1A and 1B, respectively) and $Ru(bpy)_3^{2+}$'s emission intensity increased (Figure 1C). All of these effects indicate a less polar microenvironment for these probes (16). DA^+ λ_{Max} values in the dryest PFE-SS membranes studied here (ca. 498 nm) are very similar to λ_{Max} values obtained from very dry Nafion membranes

(ca. 503 nm) (16). Reference to Table I suggests that it would be difficult to dissolve DA^+ in homogeneous solvents of low enough polarity to produce a λ_{Max} value of 499 nm. This is an interesting point because it suggests that a microenvironment which would be impossible to create in homogeneous solution can be created in the PFE-SS membrane.

As water is removed from P -SS, $Ru(bpy)_3^{2+}$'s λ_{Max} redshifted and emission intensity increased (Figures 2A and B, respectively). As noted above, the redshift indicates that, as water is removed, $Ru(bpy)_3^{2+}$ is interacting more strongly with the hydrocarbon chain material.

In contrast to the spectral changes observed for the other probes, Py's I_3/I_1, was essentially unchanged when water was removed from PFE-SS (Figure 3). This suggests that Py is located in some region of the membrane which is inaccessible to water. One possible explanation is that Py is partitioned into the polymer chain material phase which separates the ionic clusters. This seems unlikely, however, in that if Py were dissolved in a fluorocarbon phase, I_3/I_1 would be expected to close to 2.0 (19). Another possibility is that Py is partitioned into an interfacial region as described by Yeager (31). Further study of the effects of water and of counterion (16) on Py emission from PFE-SS will be required.

Conclusions

These studies have shown that the microenvironment experienced by a probe within sulfonated ionomer membranes is determined by the nature of the polymer chain material and by the membrane water content. The microenvironment can be quite dynamic, in general, becoming much less polar as water is removed from the membrane. Furthermore, these studies have shown that microenvironments can be created in the ionomer membrane

which, because of solubility limitations, would be difficult to create in homogeneous solutions. These results corroborate conclusions of analogous studies conducted on the perfluorosulfonate ionomer, Nafion (16).

Luminescence data for Ru(bpy)$_3^{2+}$ from PFE-SS suggests that chain material intrudes into the ionic cluster. This conclusion is supported by both transport (6) and spectroscopic (12) data. This is an important issue because intrusion of chain material into the cluster phase undoubtedly has the deleterious effect of retarding the rate of transport through the membrane. We are, therefore, conducting further studies of the extent of chain material penetration.

Finally, it is important to note that all of the probes studied here are relatively hydrophobic. As such, they undoubtedly seek out the more hydrophobic parts of the ionic cluster. It is not surprising, then, that these probes report back rather nonpolar microenvironments. To complement these data from hydrophobic probes, we are currently studying the emission characteristics of hydrophilic probes (e.g., lanthanide ions) in ionomer membranes.

Acknowledgement

References

1. A. Eisenberg and H. L. Yeager (eds.), "Perfluorinated Ionomer Membranes"; ACS Symposium Series No. 180, ACS, Washington, D.C., 1982.

2. A. Eisenberg (ed.), "Ions in Polymers"; ACS Advances in Chemistry Series No. 187, ACS, Washington, D.C., 1980.

3. E. Gileadi, S. Srinivasan, F. J. Salzano, C. Braun, A. Beaufrere, S. Gottesfield, L. J. Nuttal and A. B. La Conti, J. Power Sources, 1977, 2, 191.

4. T. H. Teherani, S. N. Frank and K. Carson, Presented to the Spring ACS National Meeting, April 10, 1984, St. Louis, MO.

5. F. G. Will and H. S. Spacil, J. Power Sources, 1980, 5, 173.

6. C. R. Martin and K. A. Dollard, J. Electroanal. Chem., 1983, 159, 127, and references therein.

7. S. G. Cutler, in "Ions in Polymers"; A. Eisenberg (ed.), Chap. 9. ACS, Washington, D.C., 1980.

8. E. J. Roche, M. Pineri and R. Duplessix, J. Polym. Sci. Polym. Phys. Ed., 1982, 20, 107.

9. E. J. Roche, R. S. Stein and W. J. MacKnight, J. Polym. Sci. Polym. Phys. Ed., 1980, 18, 1035.

10. H. K. Pan, D. J. Yarusso, G. S. Knapp and S. L. Cooper, J. Polym. Sci. Polym. Phys. Ed., 1983, 21, 1389.

11. B. A. Brozoski, M. M. Coleman and P. C. Painter, Macromolecules, 1984, 17, 230.

12. M. Falk, Can. J. Chem., 1980, 58, 1495.

13. N. J. Turro, M. W. Geiger, R. R. Hautala and N. E. Schore, in "Micellization, Solubilization and Microemulsions"; K. L. Mittal (ed.), p. 75. Plenum Press, NY, NY, 1977.

14. P. C. Lee and D. Meisel, J. Am. Chem. Soc., 1982, 104, 4824.

15. N. E. Prieto and C. R. Martin, J. Electrochem. Soc., 1984, 131, 751.

16. M. N. Szentirmay, N. E. Prieto and C. R. Martin, Macromolecules, Submitted.

17. V. D'Agostino, J. Lee and E. Lu, in "Ion Exchange"; R. S. Yeo and R. P. Buck (eds.), p. 148. Proceedings of the Electrochemical Society, Vol. 8-2, The Electrochemical Society, Pennington, NJ, 1981.

18. C. R. Martin and H. Freiser, Anal. Chem., 1981, 53, 902.

19. K. Kalyanasundaram and J. K. Thomas, J. Am. Chem. Soc., 1977, 99, 2039.

20. Y.-H. Li, L.-M. Chan, L. Tyler, R. T. Moody, C. M. Himel and D. M. Hercules, J. Am. Chem. Soc., 1975, 97, 3118.

21. K. Kalyanasundaram, Coord. Chem. Rev., 1982, 46, 159.

22. N. J. Turro and P. C. Lee, J. Phys. Chem., 1982, 86, 3367.

23. M. N. Szentirmay and C. R. Martin, J. Electrochem. Soc., 1984, 131, 1652.

24. C. G. Bazuin and A. Eisenberg, J. Chem. Ed., 1981, 58, 938.

25. L. Y. Levy, A. Jenard and H. D. Hurwitz, J. C. S. Faraday I, 1980, 76, 2558.

26. R. Vasquez, J. Avalos, F. Volino, M. Pineri and D. Galland, Appl. J. Polym. Sci., 1983, 28, 1093.

27. W. Y. Hsu and T. D. Gierke, Macromolecules, 1982, 15, 101.

28. K. A. Mauritz, C. J. Hora and A. J. Hopfinger, Adv. Chem. Ser., 1980, 187, 123.

29. J. Y. C. Lee, Private communication.

30. A. Eisenberg, Macromolecules, 1960, 33, 147.

31. H. L. Yeager and A. Steck, J. Electrochem. Soc., 1981, 128, 1880.

Table I. Wavelength of maximum emission intensity (λ_{Max}) for DA$^+$ and Ru(bpy)$_3^{2+}$ and I_3/I_1 for Py in various solvents.

Solvent	DA$^+$	λ_{Max} (nm) Ru(bpy)$_3^{2+}$	Py I_3/I_1
Water	571	613	0.58
Ethylene Glycol	544	--	0.79
Methanol	534	610	0.72
Ethanol	526	606	0.80
Butanol	522	608	0.94
Pentanol	519	616	0.98
Decanol	513	622	1.24
Hexane	--	--	1.50
p-Xylene	--	--	0.95

Table II. Emission Characteristics of Probes in Fully Hydrated PFE-SS and PE-SS.

Membrane	$\%H_2O$	H_2O/SO_3^-	DA^+	λ_{Max} (nm) $Ru(bpy)_3^{2+}$	PyI_3/I_1
$PFE-SS-H^+$	27	13	510	608	0.90
$PFE-SS-Na^+$	19	9	509	--	0.91[c]
$PFE-SS-K^+$	19	9	510	--	0.86[c]
$PFE-SS-Cs^+$	19	10	510	--	0.90[c]
$PE-SS-H^+$	118	46	--	628	--
$PE-SS-Na^+$	116	46	559[a]	--	--
$PE-SS-K^+$	107	44	543[a]	--	--
$PE-SS-Cs^+$	102	42	544[b]	--	--

[a]Excitation λ = 360 nm. [b]Exciation λ 380 nm. [c]Excitation λ = 335 nm.
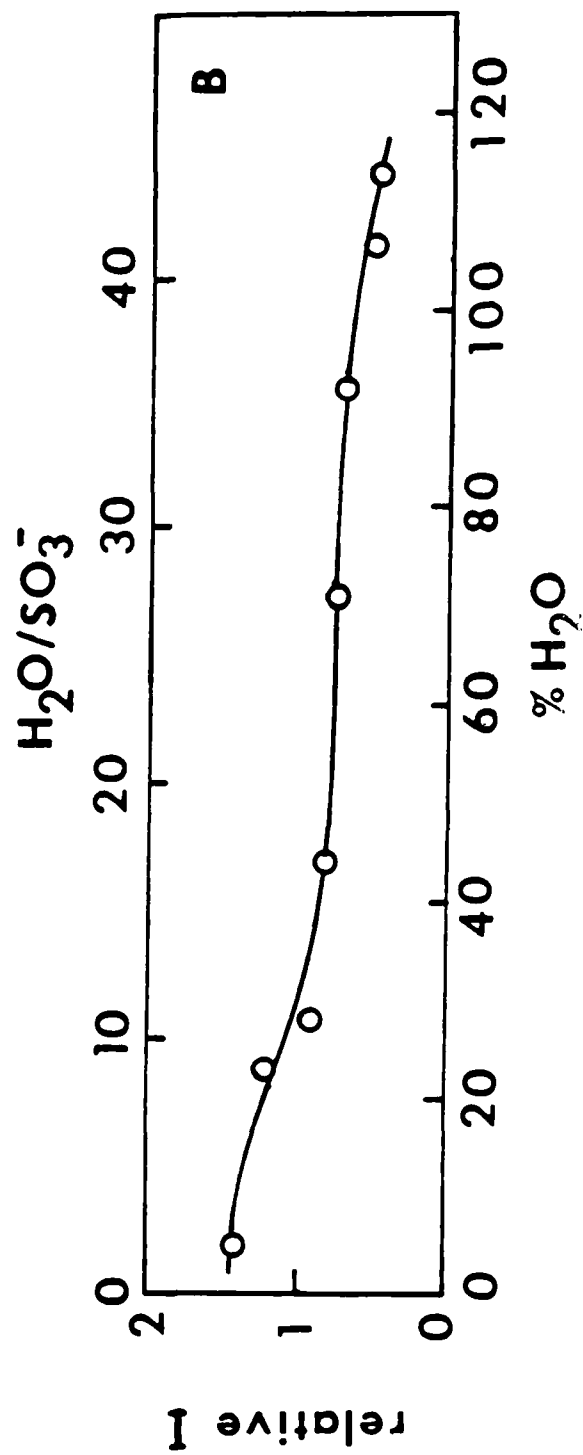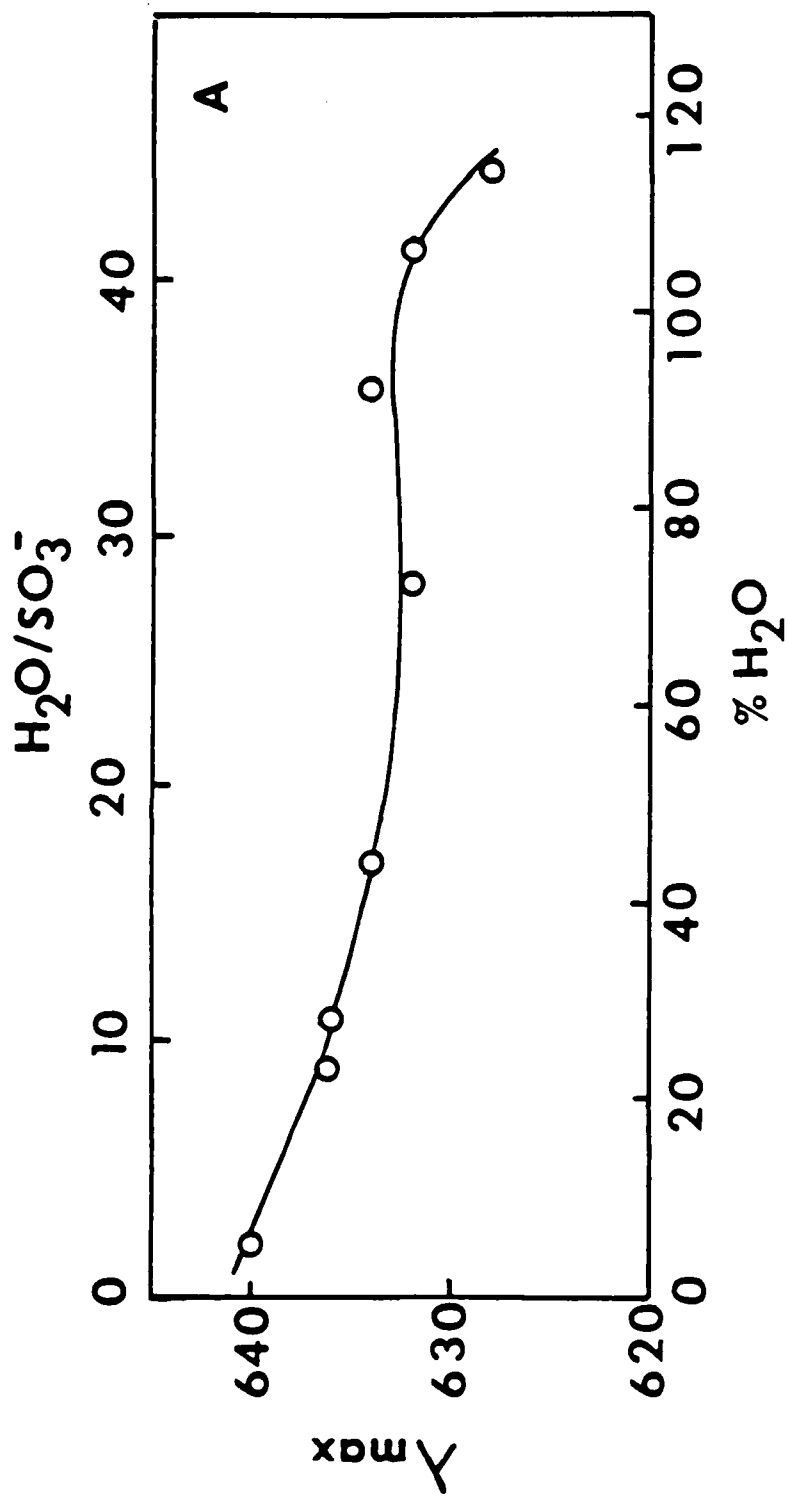
Figure Captions

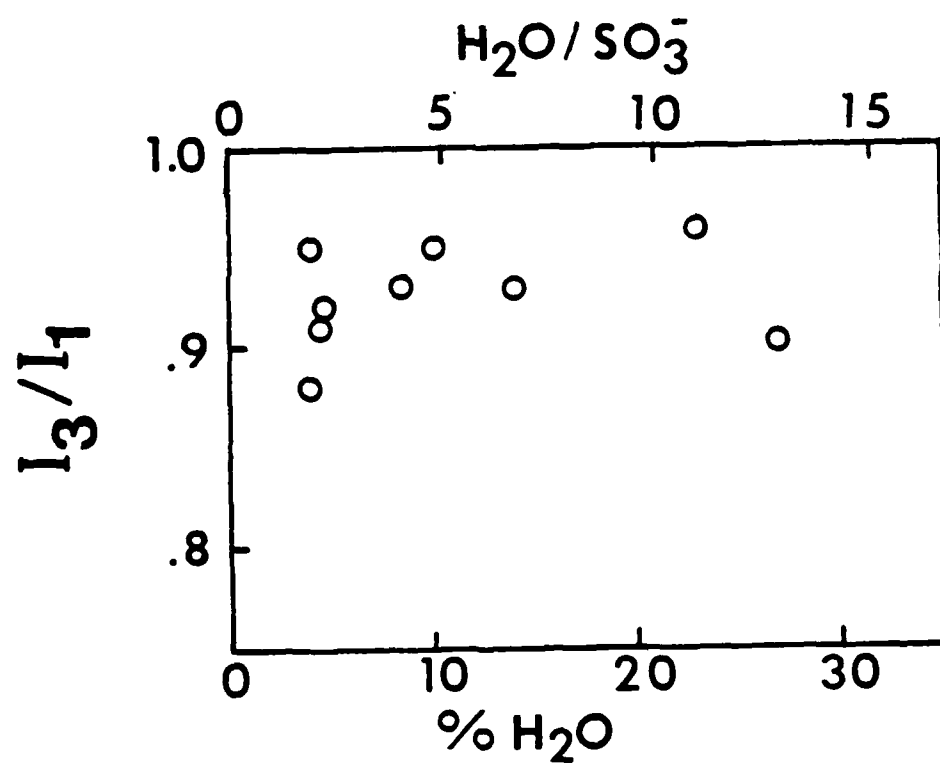Figure 1. Emission characteristics of probes vs. PFE-SS water content.
A. DA^+ λ_{Max} in Na^+ form PFE-SS. B. $Ru(bpy)_3^{2+}$ λ_{Max} in H^+ form
PFE-SS. C. $Ru(bpy)_3^{2+}$ relative intensity in H^+ form PFE-SS.

Figure 2. Emission wavelength maxima (A) and relative intensities (B) of
$Ru(bpy)_3^{2+}$ vs. water content of PE-SS, H^+ form.

Figure 3. Py I_3/I_1 vs. water content of PFE-SS, H^+ form.
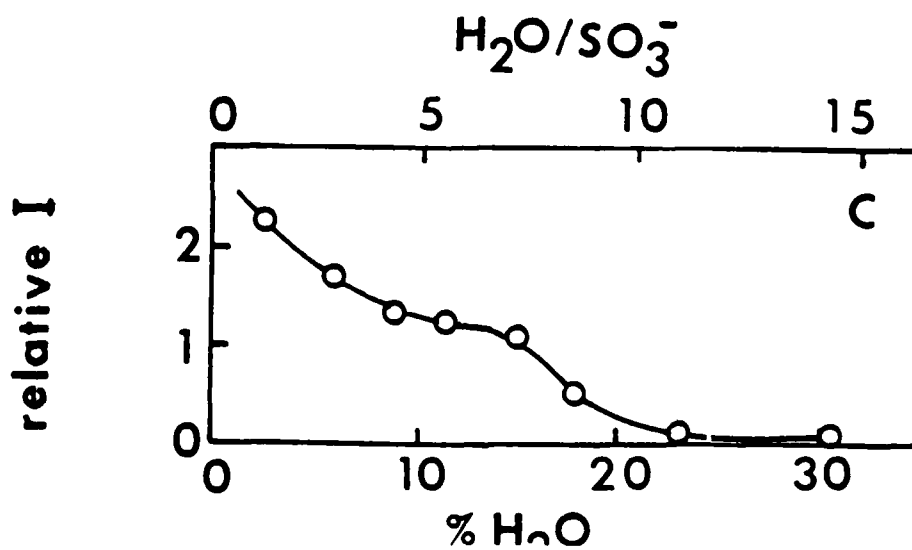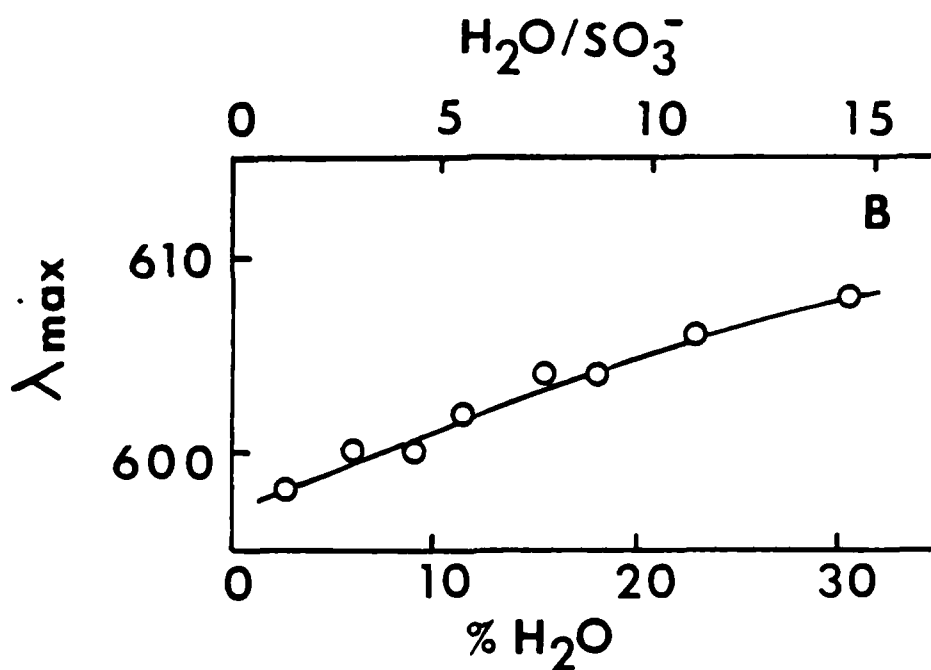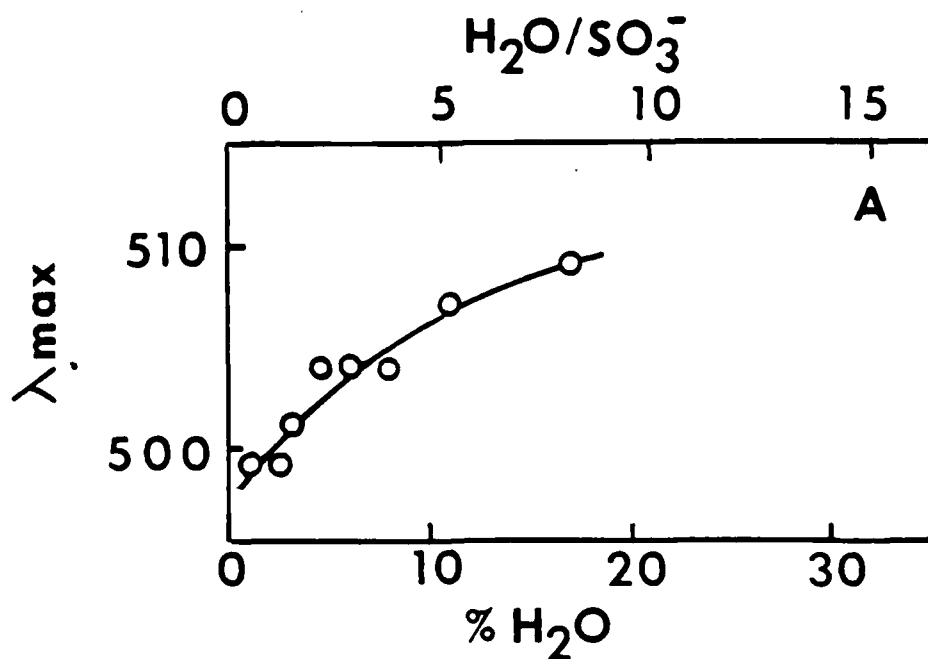
TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

END

FILMED

5-85

DTIC